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**CONCENTRATIONS OF POLYCYCLIC AROMATIC
HYDROCARBONS IN SEDIMENT AND GROUND WATER
NEAR THE WYCKOFF WOOD TREATMENT FACILITY,
WEST SEATTLE, WASHINGTON**

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ABSTRACT

Recent sediment analysis in Elliott Bay, Washington, showed elevated polycyclic aromatic hydrocarbons (PAHs) near the Wyckoff wood treating plant. For this study, additional sediment samples were taken within 200 meters of the site to determine the distribution and severity of contamination. Relative abundance of individual high weight PAHs helped identify potential sources. Concentrations of metals (As, Cr, Cu, and Zn) associated with wood preservation were also examined. Comparatively high concentrations of PAHs were found in subtidal sediments near the Wyckoff facility (total PAHs at one location exceeded 1000 ppm dry weight). Concentrations increased toward the Wyckoff Company, implying this facility is the probable source of PAHs. Seven of 16 samples exceeded the highest Apparent Effects Threshold (AET), which indicates biological problems are likely to occur at the observed PAH concentrations. PAHs, pentachlorophenol, and high concentrations of metals were found in two monitoring wells onsite, indicating migration of wood preservative into the ground water.

INTRODUCTION

Background

Surveys for contaminants in Elliott Bay sediments were conducted for EPA in 1985 (PTI & Tetra Tech, 1988). Results of that comprehensive sampling effort showed an elevation in PAHs near the Wyckoff wood treating plant on the south shore of Elliott Bay (Figure 1). Sediment bioassays demonstrated that the high levels of PAH found near the site caused significant biological effects. Contamination of marine sediments and ground water by wood preservative chemicals has occurred at wood treating facilities located near tidewater in Eagle Harbor, Washington (Yake and Norton, 1986), and Pensacola, Florida (Goerlitz, *et al.*, 1985). In addition to high concentrations of PAHs found in creosote (McNeil, 1959 in Merrill and Wade, 1985), wood treating employs other potential contaminants, including pentachlorophenol, copper, chromium and arsenic (in the formulation copper-chrome-arsenate: CCA), and zinc (Stranks, 1976).

To determine the extent and possible source of this contamination in Elliott Bay, the Northwest Regional Office (NWRO) of the Department of Ecology requested a thorough examination be conducted by the Environmental Investigations Program of the Department of Ecology. This report summarizes that investigation.

Goals and Strategy

The goal of this investigation was to determine the extent of contamination by PAHs and selected metals (As, Cr, Cu, Zn) near the Wyckoff facility. If the concentrations of these contaminants proved to be higher than local background levels, an additional goal was to determine if a link exists between elevated concentrations and operations at the Wyckoff facility.

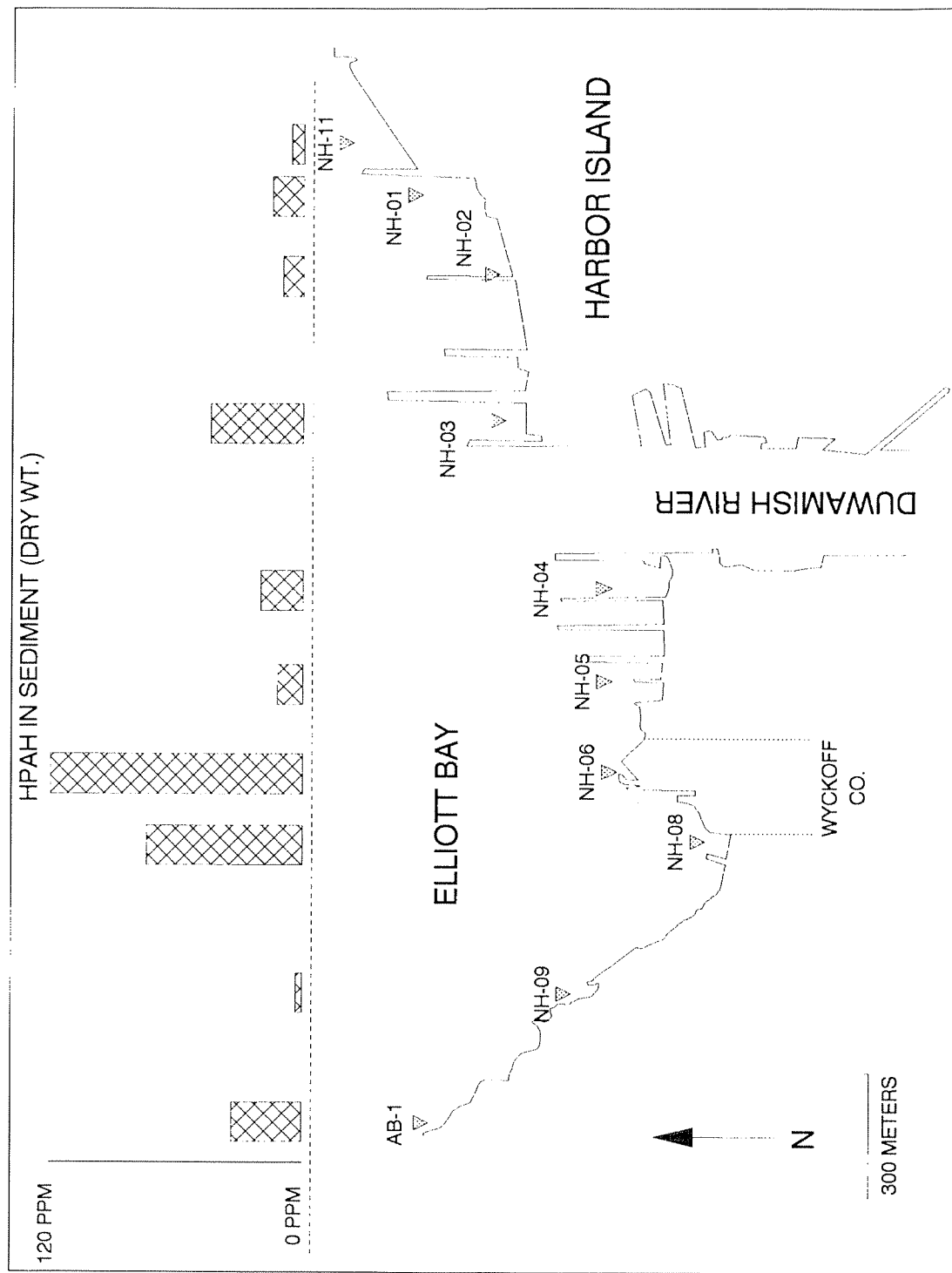


Figure 1. HPAH is sediment along south shore of Elliott Bay near the West Waterway of the Duwamish River. Data from PTI and Tetra Tech Elliott Bay Action Program.

The Wyckoff facility was evaluated as a potential source of PAHs and metal contamination in two ways. The first was based on the premise that a source of contamination may be identified by evaluating gradients in sediment contamination. The presence of a gradient was investigated by sampling a set of stations adjacent to the shore (within 10 yards) and a second set of stations greater than 50 yards offshore. The second strategy relies on the examination of ratios of individual contaminants, in this case constituent high molecular weight PAHs, to identify probable sources (i.e., petroleum, creosote, combustion products). This type of analysis has been proven useful elsewhere (Lake, *et al.*, 1979; Sporstol, *et al.*, 1983). In the present study, two samples of creosote product and two samples of ground water were sampled to examine the relative amount of each aromatic series to discern possible sources for PAH.

METHODS

Reconnaissance Survey

To roughly discern hydrocarbon distribution in sediments and to aid in sample location selection, a reconnaissance survey was conducted near the Wyckoff facility on March 17, 1988. Thirty-one bottom grabs were taken around the perimeter of the site with a hand-hauled Petite Ponar grab sampler and the sediments were visually examined for oil sheen.

Sampling Survey

Based on the overall sampling strategy and results of the reconnaissance survey, 16 locations were chosen for sediment sampling on April 21, 1988 (Figure 2). From site 8 and site 14, two samples each were sent to the laboratory as blind duplicates. Sediment samples were collected with a 0.1 m² modified Van Veen grab. Positions were located through distances from landmarks measured with an optical range measurer. For each sample, sediments not in contact with the side of the grab were spooned from the top 2 cm, placed in a stainless steel beaker, and homogenized by stirring. Subsamples for metals, base neutral acid organics, and total organic carbon (TOC) analysis were then removed and placed in 8-ounce priority pollutant-cleaned jars with teflon-lined lids (obtained from ICHEM; Hayward, California). A separate small Whirl-pak was filled with sediment for grain size analysis. Tools (spoons, beakers) were decontaminated between samples using sequential washes with Alconox detergent, distilled water, 10 percent nitric acid, pesticide-grade methylene chloride, and acetone. Samples were collected in the order of anticipated increasing contamination based on reconnaissance survey data. All samples were held in coolers on ice until delivered the following day to the laboratory.

On May 6, water samples from the bottom of two monitoring wells (1A and 3) were collected with teflon bailers decontaminated through the rinse procedure described above. Well 1A is approximately 16 feet deep, with the bottom 10 feet screened. Well 3 is 18 feet deep with the bottom 5 feet screened. Water samples were placed in 2-liter priority pollutant-cleaned jars. Two samples of creosote product were also taken into 1-liter jars at the sampling spigot between the tanks and the retorts.

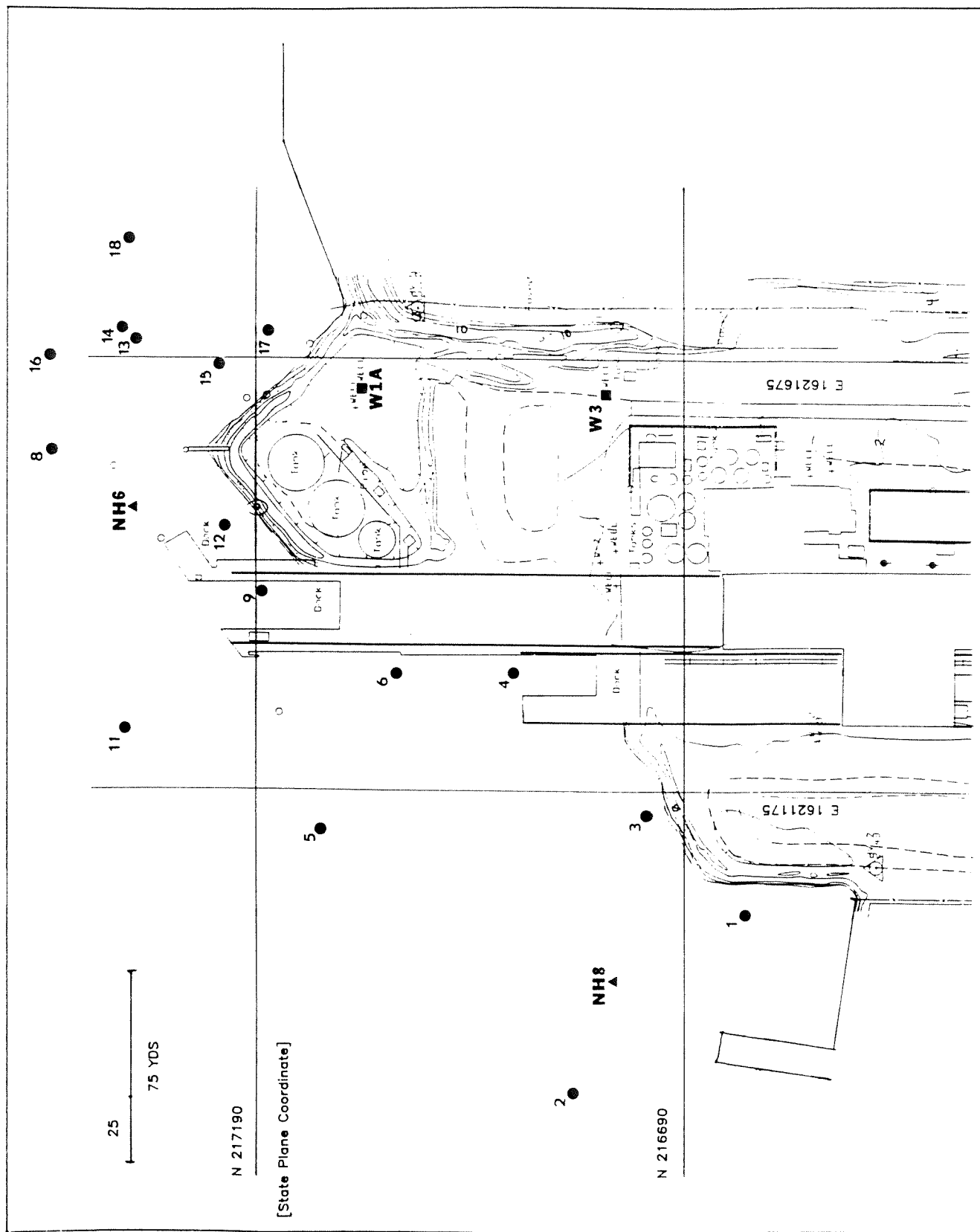


Figure 2. Location of study site and sample sites for sediments and wells (prefix "W").

Physical/Chemical Analysis

All samples were sent to the Department of Ecology/EPA Laboratory in Manchester, Washington. Aliquots for determination of semivolatile organics, grain size, and TOC were sent to Laucks Testing Laboratory in Seattle, Washington. Metals analyses were conducted at the Manchester Laboratory. Quality assurance review of the organics data was conducted by Ecology and Environment (consultants), Seattle, Washington. Field sampling methods adhered to Puget Sound Protocols (U.S. EPA; Tetra Tech, 1985).

Semivolatile organics in sediments were extracted by Method 3550 (sonication extraction; EPA, 1986) and analyzed by Method 8270 (capillary column gas chromatography with mass spectrometer detector; EPA, 1986). Internal standards used were those specified in the EPA Contract Laboratory Program (CLP) (EPA, 1984a), as well as 2 fluorobiphenyl, d14 p-terphenyl, and d10 pyrene. Although the methods used can detect pentachlorophenol, recovery can be relatively inefficient and detection limits can be high.

Semivolatile organics in water were extracted and analyzed by Method 625 (EPA, 1984b). Product was extracted by Method 3580 (EPA, 1986) (waste dilution method) and analyzed by Method 625. TOC was measured by persulfate-UV method (APHA, 1985). Grain size was measured with sieves and pipettes (Holme and McIntyre, 1971).

For metals analysis, sediments were digested using nitric acid and hydrogen peroxide, as specified in EPA Method 3050 (EPA, 1986). Copper, zinc, and chromium were analyzed on an inductively coupled plasma spectrophotometer using EPA Method 200.7 (EPA, 1982). Arsenic was analyzed on an atomic absorption spectrophotometer using Method 206.5 (EPA, 1983).

Quality Assurance

To determine precision and, to some degree, accuracy of the analytical methods, one sediment sample was divided into three subsamples. Two of these subsamples were spiked in the laboratory with known concentrations of target metals and organics, and all three subsamples analyzed. In addition, two samples were homogenized and split in the field. These samples were placed in separate jars, labeled, and submitted to the laboratory as blind duplicates.

Results of these tests of precision and accuracy follow. Table 1 reviews measurements of precision of the organics and metals analysis. Field and laboratory duplicates of all analyses had acceptable precision, as measured by relative percent difference between duplicates. Table 2 shows matrix spike recovery of selected semivolatile organics. EPA Contract Laboratory Program (CLP) (EPA, 1984a) provided guidelines to acceptable results for matrix recoveries. All recoveries were within quality control limits. Table 3 shows similar tests for metals. Arsenic and chromium were within control limits. Copper was not recovered within limits and the relative percent difference was high (200 percent). The differences within field duplicates for this metal were acceptably low (Table 1), but spike recovery was poor and, consequently, copper results are flagged with an "E" to denote they are estimated values only. Zinc had poor recovery on one matrix spike and results are similarly flagged.

Table 1. Results of blind field and laboratory duplicate analysis. Field duplicates were submitted to the laboratory as separate blind samples. Laboratory duplicates were mixed and split in the laboratory.

Field Number Lab number	Field Duplicates					Laboratory Duplicates					
	Conc. ug/kg d.wt.		RPD*	Conc. ug/kg d.wt.		RPD	Conc. ug/kg d.wt.		RPD		
	W7	W8		W14	W19		W5	W17			
188136	188137	188137	188143	188148		18134MS	188134MSD	188146MS	188146MSD		
CHEMICAL											
Acid/Base/Neutrals											
Dibenzofuran	840	910 J	8	5100 J	6700 J	27	450 U	170 J	3100 J	2500 J	
2-methylnaphthalene	300 J	340 J	13	52000 U	55000 U	--	44 J	68 J	1600 J	1000 J	
Naphthalene	1000	1100	10	12000 J	22000 J	59	79 J	100 J	3700 J	2600 J	
Acenaphthylene	510	270 J	62	3000 J	55000 U	--	22 J	30 J	31	37000 U	
Acenaphthene	1300	1300	0	6900 J	9400 J	31	450 U	440 U	--	37000 U	
Fluorene	1100	1200	9	6700 J	9200 J	31	170 J	240 J	34	37000 U	
Phenanthrene	4500	5200	14	27000 J	31000 J	14	680	750	10	13000 J	
Anthracene	2100	1500	33	29000 J	22000 J	27	310 J	350 J	12	18000 J	
Sum LPAH**	10500 J	10600 J	1	84600 J	93600 J	10	1260 J	1470 J	15	34700 J	
Fluoranthene	6000	5900	2	120000	84000	35	1300	1500	14	41000	
Pyrene	14000 R	15000 R	7	200000	120000	50	450 U	450 U	--	37000 U	
Benzo (a) anthracene	5000	5600	11	130000	72000	57	550	930	51	17000 J	
Chrysene	3900	5500	34	110000	80000	32	550	740	29	28000 J	
Benzofluoranthenes	11000	10000	10	127000 J	98000	26	640 J	920 J	36	23800 J	
Benzo (a) pyrene	4200	4900	15	47000 J	39000 J	19	290 J	380 J	27	10000 J	
Indeno (1,2,3-cd) perylene	1600	1900	17	22000 J	11000 J	67	88 J	110 J	22	37000 U	
Dibenzo (a,h) anthracene	460 J	420 J	9	52000 U	55000 U	--	450 U	450 U	--	37000 U	
Benzo (g,h,i) perylene	1300	1500	14	15000 J	11000 J	31	86 J	110 J	24	3500 J	
Sum HPAH**	46500 J	49700 J	7	771000 J	515000 J	40	3500 J	4690 J	29	123000 J	
Metals											
Arsenic	7.7	5.2	39	14.8	14.0	6					
Chromium	28.7	23.6	20	69.4	72.6	5					
Copper	56.0	55.0	2	198.0	165.0	18					
Zinc	106.0	96.0	10	298.0	304.0	2					

* RPD = Relative percent difference = $((x-y)/(x+y/2))*100$ where x and y are replicate analyses (excludes "U" values).

** Sum excludes "U" values and are, thus, minimums, LPAH sum excludes 2-methylnaphthalene.

Qualifiers:

J = Estimate: chemical found but at less than Contract Required Detection Limit

U = Estimated sample quantitation limit (compound not found above this concentration)

R = Values from diluted injection (initial injection was unacceptable)

Table 2. Quality assurance results showing percent recovery of matrix spikes (MS) and matrix spike duplicates (MSD) of selected semivolatatile organics. Organic spike was added to samples numbers shown below at concentrations between 180 and 375 ppm.

Chemical	Percent Recovery								*RPD		
	Lab number =				QC Limits				188134 188146 QC Limits		
	MS	MSD	188134	188146	MS	MSD	188146	QC Limits (Min-Max)	188134	188146	QC Limits
Phenol	51	49	49	57	57	57	26-90	4	0	35	
2-Chlorophenol	52	49	49	63	65	65	25-102	6	3	50	
1,4-Dichlorobenzene	56	51	51	59	61	61	28-104	9	3	27	
N-Nitroso-di-n-prop.	55	54	54	69	63	63	41-126	2	9	38	
1,2,4-Trichlorobenzene	59	54	54	67	66	66	38-107	9	2	23	
4-Chloro-3-methylphenol	67	66	66	74	64	64	26-103	2	14	33	
Acenaphthene	63	62	62	63	67	67	31-137	2	6	19	
4-Nitrophenol	67	72	72	52	51	51	11-114	7	2	50	
2,4-Dinitrotoluene	56	54	54	57	62	62	28-89	4	8	47	
Pentachlorophenol	83	82	82	65	66	66	17-109	1	2	47	
Pyrene	54	65	65	60	63	63	35-142	18	5	36	

*RPD = Relative percent difference = $((x-y)/(x+y/2))*100$ where x and y are replicate analyses.

Table 3. Quality assurance results showing percent recovery of matrix spikes (MS) and matrix spike duplicates (MSD) of metals.

	Percent Recovery					*RPD	
	188138 MS	188138 MSD	188146 MS	188146 MSD	QC Limits (Min-Max)	188138	188146
Arsenic	92	77	81	78	65-135	18	4
Chromium	90	93	--	--	65-135	3	-
Copper	0	15	--	--	65-135	200	-
Zinc	110	151	--	--	65-135	31	-

*RPD = Relative percent difference = $((x-y)/(x+y/2))*100$ where x and y are replicate analyses.

Results of the organics quality assurance review showed the data are acceptable for use except where flagged with data qualifiers which modify the usefulness of the individual values. GC/MS tuning, initial calibration, continuing calibration, and surrogate recovery all were within CLP requirements. The most common reason for flagging organics data is that compounds were found and quantified at concentrations below the contract required quantitation limit (CRQL) (reported concentrations have been corrected for dilutions and percent moisture). The flag for this case is "J". CRQL is 330 ug/kg for most organics in low level analyses before correction for percent moisture and dilutions. Medium level analysis, used for highly contaminated areas, has a CRQL of 19,800 ug/kg.

RESULTS AND DISCUSSION

Grain Size and TOC

Table 4 shows TOC and grain size distribution of sediments. Sediments were primarily sandy (40-90 percent) with varying (8-50 percent) amounts of silt. Four samples had slightly more silt than sand. The clay fraction was relatively small. TOC ranged from 0.7 to 9.4 percent.

Semivolatile Organics

Table 5 shows concentrations of all semivolatile target compounds found above detection limits in the sediments surrounding the Wyckoff facility. Target compound detection limits are shown in the Appendix. The primary compounds detected were polycyclic aromatic hydrocarbons (PAHs). Diethylphthalate and dibenzofuran were also quantified. Two other phthalates were found, but because they were also found in method blanks, results are flagged in the table with a "B."

Table 6 reports results from monitoring wells 1A and 3, as well as PAH constituents found in product (creosote) used at the site. In ground water samples, the primary contaminants were PAHs. Phthalates were detected in method blanks; thus, concentrations found in samples may reflect laboratory contamination. Earlier sampling during drilling of monitoring wells on the Wyckoff site found PAHs and chlorophenols in well corings (Woodward and Clyde, 1985). In this study, pentachlorophenol was detected in one well.

PAH concentrations in sediments varied greatly between sites. Sample 13 had the highest concentration of PAHs, at over 0.1 percent total PAHs on a dry weight basis. The adjacent sample (14) also had high PAHs. Figure 3 portrays concentrations of total PAHs by location. Exceptionally high levels of PAHs were also found underneath the barge offload area (sample site W-9) where treated poles are loaded onto barges. High concentrations were also found in samples adjacent to the northeast border of the Wyckoff property. These sites are all within approximately 50 yards of the shore and 75 yards of the creosote tanks on the Wyckoff property. Generally, sites in deeper water (over 30 feet deep) or more distant from the creosote tanks had lower levels.

Table 4. Sediment characteristics (percent total organic carbon (TOC), percent sand (>62um), silt (<62um >4um) and clay) at Wyckoff subtidal sample sites.

SITE	Percent			
	TOC	Sand	Silt	Clay
W1	2.4	64.6	30.2	5.2
W2	2.3	58.6	32.7	8.7
W3	2.4	67.7	27.3	5.0
W4	0.7	90.2	7.8	2.0
W5	0.9	89.4	8.8	1.8
W6	2.2	88.9	9.5	1.6
W7	2.6	61.0	31.8	7.2
W9	4.0	68.0	28.0	4.0
W11	1.5	71.9	22.1	6.0
W12	1.1	78.5	18.3	3.2
W13	9.3	46.5	47.4	6.1
W14	7.7	42.6	49.4	8.0
W15	5.0	69.5	26.9	3.6
W16	5.5	39.8	48.4	1.8
W17	2.8	73.2	22.5	4.3
W18	9.4	41.1	49.7	9.2

Table 5. Summary of semi-volatile organics compounds detected in surface sediments collected near Wyckoff Company in Elliott Bay, WA. All values in ug/kg dry weight.

Station number Lab number	W1 188130D	W2 188131	W3 188132D	W4 188133	W5 *	W6 188135	W8 **	W9 188138	W11 188140	W12 188141	W13 188142	W14 **	W15 188144	W16 188145	W17 *	W18 188147
Acid/Base/Neutrals																
bis(2-Ethylhexyl)phthalate	1900B	250B	890B	94B	78B	160B	110B	6500B	130B	140B	9200B	8750B	6600B	570B	4267B	630B
Diethylphthalate	140J															
Di-n-butylphthalate	150J	610J	1700J	160J	180J	150J	875J	4300B	350J	300J	14000J	11000B	3600B	1000J	4333B	2700J
Dibenzofuran		260J	1000J	50J	50J	63J	320J	2000J	190J	130J	7700J	5900J			3200J	2700J
2-methylnaphthalene		260J	1600J	160J	88J	150J	1050	3500J	530	450J	33000J	17000J	10000J	1800J	4433J	1300J
Naphthalene	94J	570J	310J	100J	25J	160J	390J		350J	340J		3000J				4900
Acenaphthylene	220J	780J	2200J	220J	240J	180J	1300		410J	420J	20000J	8150J	5600J	1800J	4500J	5000
Fluorene	260J	1200J	2700	230J	227J	230J	1150	2000J	590	410J	19000J	7950J	7400J	1700J	4050J	5200
Phenanthrene	1900J	6000	13000	1400	777	1500	4850	10000J	2200	2200	60000	29000J	23000J	9200	12900J	21000
Anthracene	400J	2800	9800	840	313J	680	1800	7500J	2400	1300	48000J	25500J	28000J	9200	16333J	15000
Sum LPAH***	2960J	11600J	29600J	2950J	1700J	2900J	10500J	23000J	6480J	5120J	180000J	90600J	74000J	23700J	42200J	53500J
Fluoranthene	2800	9900	16000	2400	1333	3900	5950	110000	2100	2500	260000	102000	88000	17000	36333J	24000
Pyrene	2300J	8000	13000	1700	1300	2500	14500R	94000	2900	4000	160000	160000	120000	16000	7667J	27000
Benzo (a) anthracene	1300J	5200	7200	870J	737	1700	5300	43000	2300	2500	120000	101000	73000	19000	18000J	23000
Chrysene	1400J	5500	7500	1300	637	1600	4700	30000J	1800	1900	120000	95000	71000	29000	27000J	31000
Benzo(a)anthracenes	2700J	9700	10700	1500	790J	2650	10500	45000J	6200	7300	130000J	112500J	65000J	30000	24367J	38000
Benzo (a) pyrene	1200J	4200	4800	580J	330J	910	4550	16000J	2100	2400	46000J	43000J	24000J	13000	10500J	16000
Indeno (1,2,3-cd) perylene	570J	1500	1400J	260J	103J	330J	1750	6700J	1700	1000	19000J	16500J	9700J	3900J	2767J	5000
Dibenzo (a,h) anthracene		460J	450J			110J	440J		470J	320J				1400J		1900J
Benzo (g,h,i) perylene	610J	1100J	1300J	200J	105J	250J	1400	5300J	1400	890	13000J	13000J	6600J	3000J	3600J	3800J
Sum HPAH	12900J	45600J	62300J	8810J	5340J	13900J	49100J	350000J	21000J	22800J	868000J	643000J	457000J	132000J	130000J	170000J

* Mean of 3 analyses (matrix, matrix spike, and matrix spike duplicate, except for Acenaphthene and Pyrene, the two spiked PAH compounds)

** Mean of 2 blind field duplicates

*** Excludes 2-Methylnaphthalene

Data Qualifiers

B = Chemical found in method blank

J = Estimate due to concentration less Contract Required Detection Limit

R = Data from diluted re-injection (initial injection unacceptable)

Table 6. Concentrations of PAHs in well water and creosote from the Wyckoff facility in West Seattle. Only those compounds quantified are shown.

Field Number Lab number	ug/l (ppb)		mg/l (ppm)	
	Well 1A 97551	Well 3 97552	CREO1 97554	CREO2 97555 (Creosote)
Acid/Base/Neutrals				
bis(2-Ethylhexyl)phthalate	25JB	80B	290B	280B
Pentachlorophenol		160		
Dibenzofuran	530	53	26000	25000
2-methylnaphthalene	54J	11	66000	59000
Naphthalene	110J	150	22000	22000
Acenaphthylene			1500J	1500J
Acenaphthene	610	94	35000	34000
Fluorene	940	75	27000	25000
Phenanthrene	1900	270	67000U	66000U
Anthracene	1000	43	22000U	22000U
Sum LPAH*	4560	632	85500	82500
Fluoranthene				
Pyrene	1000	220	35000	37000
Benzo (a) anthracene	520	190	26000	24000
Chrysene	160	65	6600	6100
Benzofluoranthenes	210	66	6700	6400
Benzo (a) pyrene	108J	57J	4500J	4200J
Indeno (1,2,3-cd) perylene	42J	28J	2100J	1900J
Benzo (g,h,i) perylene		10J	530J	480J
Sum HPAH	2040	8J	380J	340J
		644	81810	80420

* = Excludes 2-methylnaphthalene and "U" values

B = Chemical found in method blank

J = Estimate due to concentration less than Contract Required Detection Limit

U = None found at detection limit shown

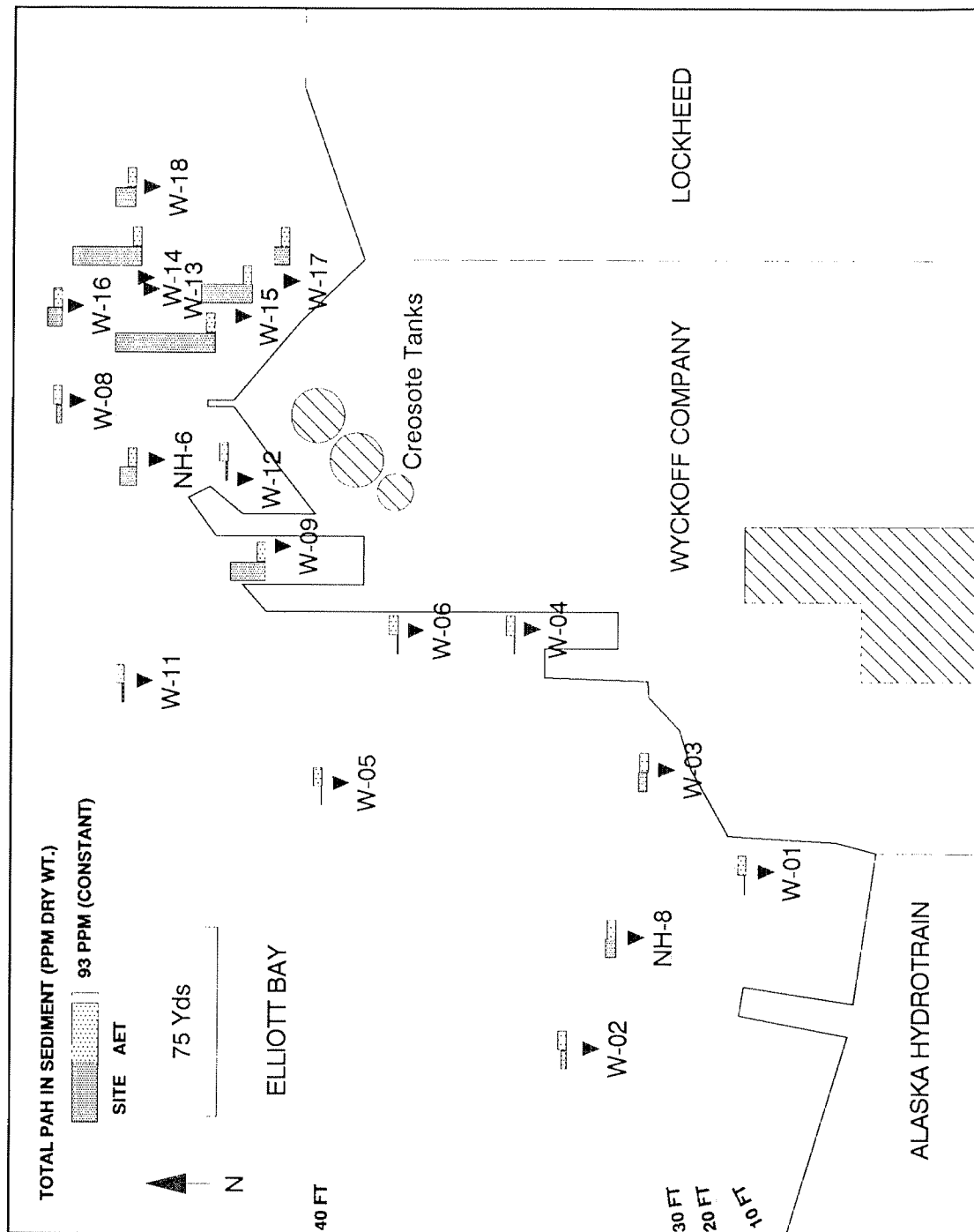


Figure 3. Concentrations of total polycyclic aromatic hydrocarbons (PAH) in sediment compared with the Amphipod Apparent Affects Threshold (see text for explanation of Apparent Effects Threshold).

Correlations between grain size distribution and PAH and metal concentrations are presented in Table 7. Total PAH correlates strongly with percent TOC. Non-polar compounds such as PAHs would be expected to sorb more readily to other carbonaceous compounds in the sediment. Also, because PAHs are organic compounds, they may have similar sources and sinks as TOC. To reveal possible patterns of PAH distribution, concentrations were normalized to percent TOC and isoconcentration lines were modeled with a kriging algorithm, plotted and shown in Figure 4. Though these contours are models and are not strictly descriptive of the concentrations found in all sediments, they do illustrate areas of highest contamination. These areas are to the northeast and northwest (Figure 4) of the Wyckoff creosote tanks and suggest, through their close proximity, a source in the vicinity of the creosote tanks. However, a spill might have contributed to high concentrations, as creosote is loaded by barge to the Wyckoff facility off the docks on the north side of the site.

Constituents Identification

Figure 5 shows relative concentrations of high molecular weight PAHs plotted on a site map. The characteristic profile of creosote is shown and clearly matches samples from onsite wells, thus providing some evidence that PAHs sampled in these wells derive from creosote. Samples W-9 and W-13 are more similar to these profiles than to background profiles (upper left corner of figure), with high relative concentrations of fluoranthene, moderate concentrations of benzo-anthracene, and low levels of benzo-fluoranthene. Sites W-2, W-1, W-8, and W-11 match background profiles as shown in the legend. These are indicated by relative enrichment of benzo-fluoranthenes. Other sites are intermediate between background and creosote. Different solubilities and degradation rates of different PAHs, as well as variation in the accuracy of laboratory analysis, may confound this type of analysis. However, patterns seen here appear to be consistent with the hypothesis that creosote from the Wyckoff facility is responsible for elevation of PAH concentrations in sediments adjacent to the facility.

Metals

Metals concentrations in sediments and monitoring well water are listed in Table 8. All metals values in sediments co-varied with each other. Samples W-1, W-9, and W-17 had the highest concentrations. These sites are adjacent to the Wyckoff facility. W-1 is near an 18-inch diameter storm sewer outfall that drains Seattle Steel and receives ground water infiltration from Harbor Island landfill (D. Cargill, Department of Ecology, 1988). Arsenic is found at relatively high concentrations near the site and to the northwest of the site at the outer tier of samples.

Arsenic concentrations correlated with total PAH, percent TOC, and percent fines ($P = .05$; see Table 7). If arsenic is corrected for TOC, levels are highest on the east side of the site. If arsenic is corrected for percent fines, most of the arsenic is found to the northwest of the site. All four metals were found in monitoring well samples. Metals concentrations found in ground water were high, suggesting some leachate from treated timbers stored on site.

Table 7. Pearson correlation coefficients between concentrations and properties of soils (silt < 62um and > 4 um, clay <4um, TOC = Total organic carbon, TOTPAH = total polycyclic aromatic hydrocarbon).

	Silt	Clay	TOC	TOTPAH	AS	CR	CU
Clay	0.864**						
TOC	0.860**	0.561+					
TOTPAH	0.601+	0.196	0.794**				
AS	0.733*	0.493	0.677*	0.533+			
CR	0.667+	0.437	0.660+	0.483	0.913**		
CU	0.404	0.197	0.321	0.286	0.861**	0.710*	
ZN	0.677*	0.447	0.573	0.446	0.942**	0.825**	0.904**

+ p<0.05
 * p<0.005
 ** p<0.001

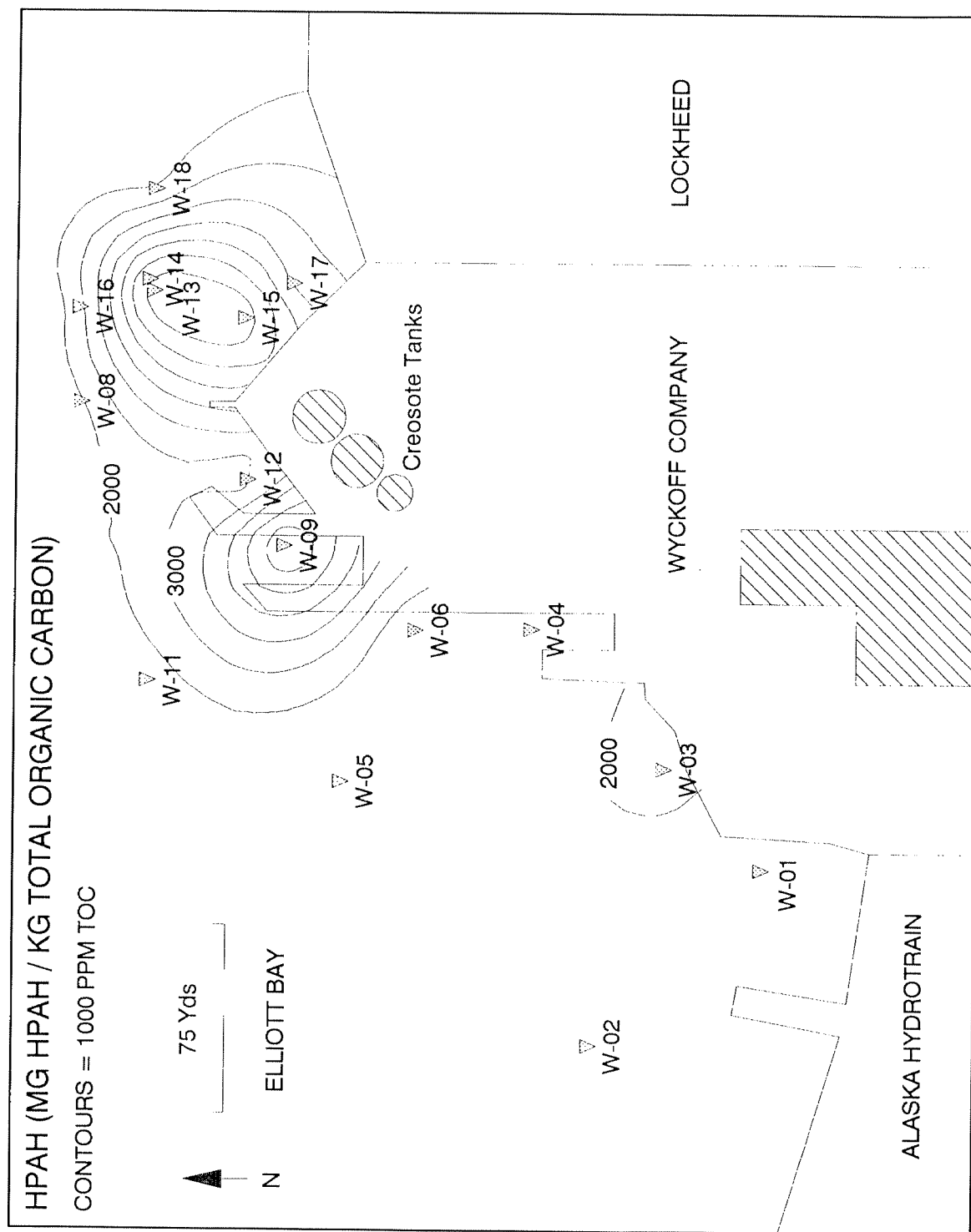


Figure 4. High molecular weight PAH concentrations in sediments modelled through Kriging near the Wyckoff facility.

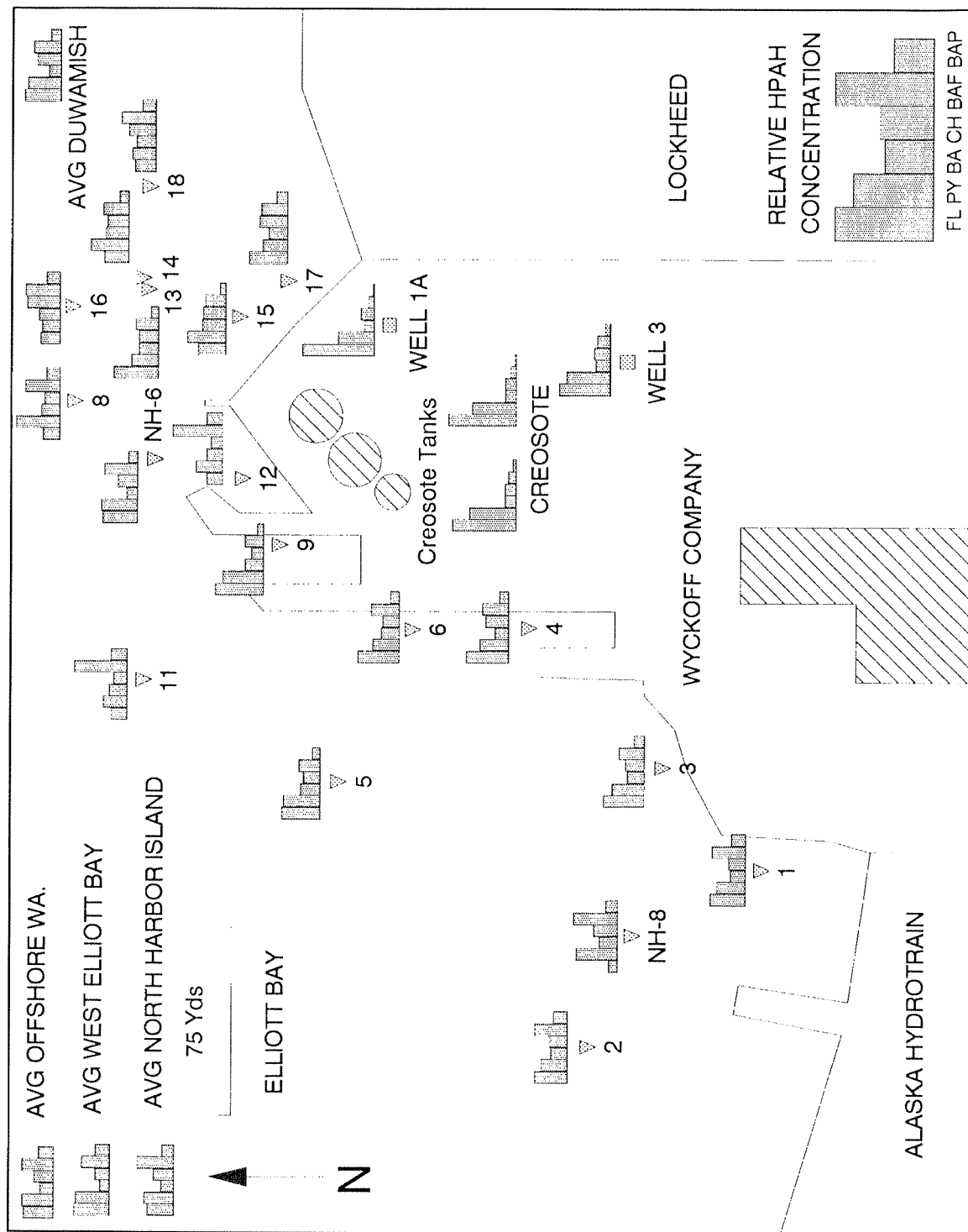


Figure 5. Relative concentrations of high molecular weight PAH concentrations in sediments, wells, and product. Bars represent individual HPAH compounds as a percentage of total HPAH concentrations for each site. (FL=Fluoranthene, PY=Pyrene, BA=Benzo-Anthracene, CH=Chrysene, BAP=Benzo-a-fluoranthene, BAP=Benzo-a-pyrene).

Table 8. Metals concentrations in
subtidal sediments and
well water, Wyckoff facility,
Elliott Bay.

SITE	Concentration ug/g dry wt			
	AS	CR	CU	ZN
W1	14.6	77.3	319E	345E
W2	7.6	33.2	111E	204E
W3	7.9	46.2	197E	248E
W4	2.8	11.1	37E	81E
W5	3.0	7.3	21E	56E
W6	2.3	13.3	35E	64E
W7	6.5	26.2	55E	101E
W9	14.5	38.8	355E	342E
W11	4.9	22.5	65E	112E
W12	5.4	22.1	52E	183E
W13	12.6	68.4	152E	252E
W14	14.4	71.0	181E	301E
W15	10.6	61.7	149E	232E
W16	12.1	54.5	155E	263E
W17	15.3	97.1	266E	279E
W18	14.4	83.2	170E	299E
Concentration ug/l				
Well 1a	46	-	150E	97E
Well 3	385	145	1140E	1860E

E = Estimate due to failure of one or
more quality control tests

Biological Effects

Toxicity criteria for marine sediments have been developed using data from contaminant analyses and bioassays, interpreted with the Apparent Effects Threshold (AET) principle (PTI, 1988). Simply stated, the AET for a given contaminant is the level above which deleterious biological effects are always seen. These biological effects are measured by four parameters: amphipod, oyster larvae, microtox bacteria bioassays, and benthic species abundance. Each method yields a separate AET estimate. All determinations are controlled through measurements at areas distant from industrial activity and contamination. Data from 50 to 200 stations in Puget Sound are available to assay AET levels for most priority pollutants. Table 9 shows the AET concentrations for chemicals found in this study. Clearly, several sites exceeded the highest AET for PAHs, as illustrated earlier in Figure 3. A model of the areal distribution of sediments that exceeded the highest AET is shown in Figure 6. Metals concentrations did not exceed AETs.

Comparison to Other Areas

Concentrations of PAHs in sediments found in this study exceed all but one site reported in several other studies in Puget Sound. Table 10 compares median, 90th percentile, and maximum concentrations from other studies with concentrations found in this study. Analyses of 170 to 210 Puget Sound sediment samples are reviewed in the Pollutants of Concern Matrix (Tetra Tech, 1986a). Results are divided into relatively unpolluted and more contaminated areas. The more contaminated areas are referred to in the Matrix and in Table 10 as "non-reference" areas. Samples from Elliott Bay and Eagle Harbor (an EPA designated "Superfund" site; n = 131), reported after the Matrix was published (Tetra Tech, 1988; Tetra Tech, 1986b), are also compared to Wyckoff samples in Table 10.

Median concentrations at Wyckoff exceed the 90th percentile for 13 of 14 PAHs measured at all other sites. Minimum concentrations found in this study exceed the median for other areas for 10 of 15 PAHs. Note that sites which form the comparison are not "pristine" or control sites. They are urban sites located near multiple sources of contamination. Table 11 shows the 15 sites from this study, Eagle Harbor, and Elliott Bay that have the highest concentrations of total PAHs. Of the 15, nine are located near the Wyckoff facility in Elliott Bay.

Table 9. Puget Sound Apparent Effects Threshold (AET) concentrations in sediments of semi-volatile organics (ug/kg normalized to dry weight) and metals (mg/kg normalized to dry weight) compared to concentrations found in sediments near Wyckoff Company. Source: PTI, 1988.

Chemical	AET				Wyckoff Sediment Samples			
	Amphipod	Oyster	Benthic	Microtox	Geo. Mean	Range		Exceed AET*
						Low	High	
Acid/Base/Neutrals								
Dibenzofuran	1700	540	700	540	850	150	14000	5
2-methylnaphthalene	1900	670	1400	670	392	50	7700	1
Naphthalene	2400	2100	2700	2100	1189	88	33000	6
Acenaphthylene	1300	>560	1300	>560	285	25	3000	2
Acenaphthene	2000	500	730	500	1254	180	20000	6
Fluorene	3600	540	1000	540	1403	227	19000	5
Phenanthrene	6900	1500	5400	1500	6267	777	29000	8
Anthracene	13000	960	4400	960	4101	313	28000	5
Sum LPAH**	24000	5200	13000	5200	15115	1670	180000	5
Fluoranthene	30000	25000	24000	1700	12991	1333	260000	4
Pyrene	16000	3300	16000	2600	12877	1300	160000	4
Benzo (a) anthracene	5100	1600	5100	1300	8275	737	120000	10
Chrysene	9200	2800	9200	1400	8487	637	120000	7
Benzo(a)fluoranthenes	7800	3600	9900	3200	12765	790	130000	9
Benzo (a) pyrene	3000	1600	3600	1600	5015	330	46000	7
Indeno (1,2,3-cd) peryl	1800	690	2600	600	1971	103	19000	7
Dibenzo (a,h) anthracene	540	230	970	230	502	110	1900	2
Benzo (g,h,i) perylene	1400	720	2600	670	1605	105	13000	7
Sum HPAH**	69000	17000	69000	12000	66898	5335	868000	7
Metals								
Arsenic	93	700	57	700	7.9	2.3	15.3	0
Chromium	270	--	260	--	36.1	7.3	97.1	0
Copper	1300	390	530	390	108.4	21.0	355	0
Zinc	960	1600	410	1600	181.5	56.0	345	0

* Number of samples that exceeded highest AET value.

**Sums are calculated by site; they are not totals of values in this table

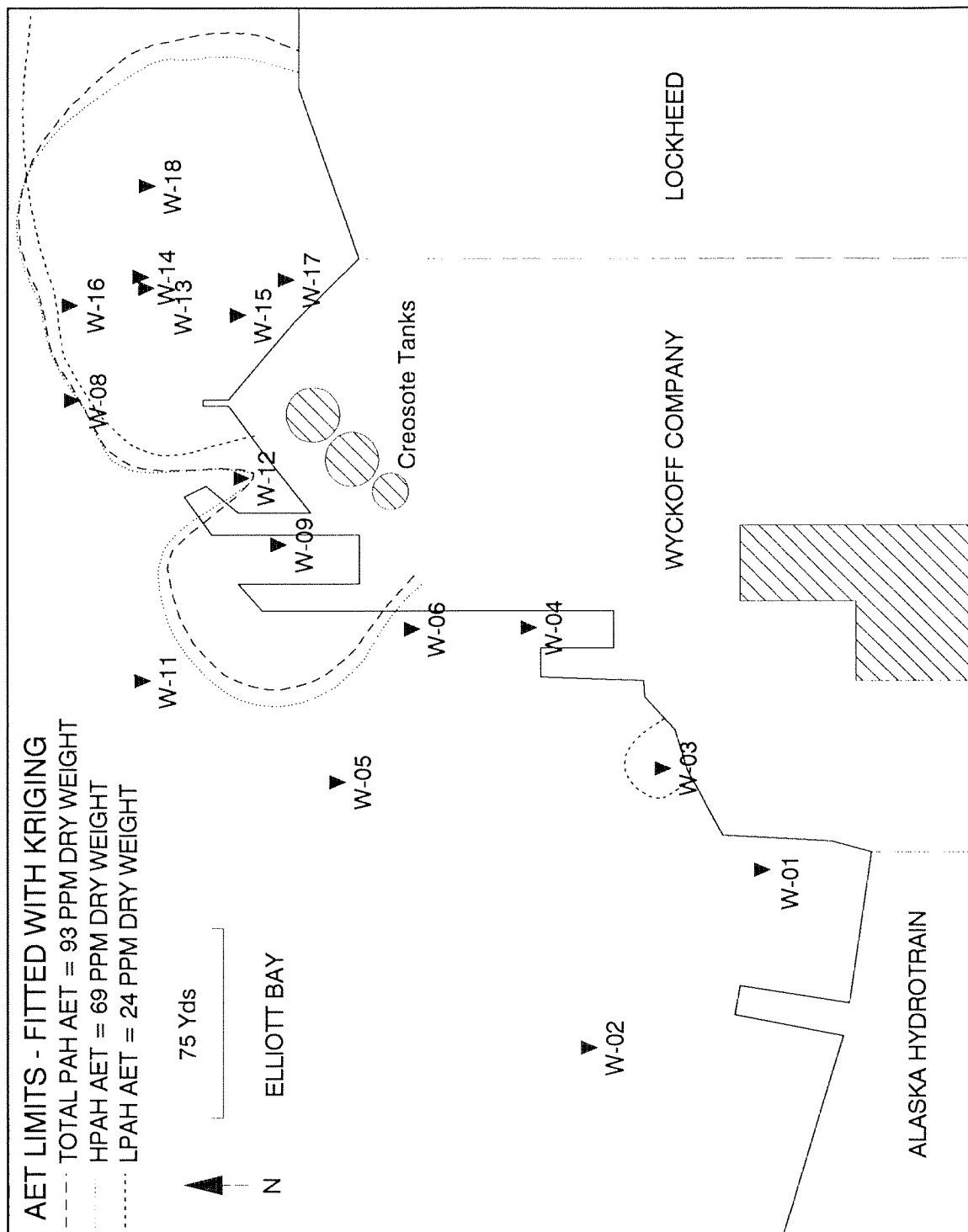


Figure 6. Amphipod Apparent Affects Threshold borders modelled through Kriging near the Wyckoff facility based on sediment samples.

Table 10. Comparison of concentrations of several chemicals found in sediments near the Wyckoff Facility in West Seattle with concentrations in other areas of Puget Sound.

Chemical	Elliott Bay and Eagle Harbor			Non-Reference Area			Wyckoff Sediment Samples		
	Median	90th Percentile	Maximum	Median	90th Percentile	Maximum	Minimum	Median	Maximum
Acid/Base/Neutrals (sediment ug/kg dry weight)									
Dibenzofuran				130	380	2000	150*	745**	14000
2-Methylnaphthalene				110	410	1200	50	130	7700
Naphthalene	42	810	15000	200	1200	5900	88	1325**	33000
Acenaphthylene	15	1400	37000	56	350	4000	25	130	3000
Acenaphthene	14	600	33000	71	460	3300	180*	990**	20000
Fluorene	52	860	37000	91	460	4800	227*	1450**	19000
Phenanthrene	740	3300	330000	290	1300	34000	777*	7600**	29000
Anthracene	270	2600	190000	110	530	9960	313*	5150**	28000
LPAH	1310	8900	630000	850	4400	55000	1670*	17305**	180000
Fluoranthene	1200	9400	1300000	530	2300	71000	1333*	13000**	260000
Pyrene	1200	7600	740000	630	2200	63000	1300*	10500**	160000
Benzo(a)anthracene	520	3100	300000	530	2300	71000	737*	6150**	120000
Chrysene	800	5500	350000	420	2000	35000	637*	6500**	120000
Total benzofluoranthenes	930	7700	300000	710	3600	29000	790*	10100**	130000
Benzo(a)pyrene	390	3200	100000	350	1700	23000	330	4675**	46000
Indeno(1,2,3,c,d)pyrene	230	1800	40000	170	840	9100	103	1725**	19000
Dibenzo(a,h)anthracene	17	710	12000	52	450	4000	110*	-	1900
Benzo(g,h,i)perylene	180	1500	32000	180	1300	11000	105	1400**	13000
HPAH	5900	40000	3200000	3400	17000	250000	5335*	54970**	868000
Metals (sediment mg/kg dry wt)									
Arsenic	9.9	36.2	584	11.0	39.0	9700	2.3	9.2	15.3
Chromium	85	194	1080	31.0	66.0	130	7.3	42.5	97.1
Copper	77.8	248	2050	55.0	90.0	11000	21.0	150.5**	355
Zinc	35.4	57.8	366	27.0	51.0	120	56.0*	240.0**	345

* Minimum at Wyckoff exceeds median for for all Elliott Bay, Eagle Harbor, and Puget Sound non-reference areas.

** Median at Wyckoff exceeds 90th percentile for all Elliott Bay, Eagle Harbor, and Puget Sound non-reference areas.

Notes: Eagle Harbor is on EPA's designed "Superfund" site. Non-reference areas refer to sites in Puget Sound that are considered highly contaminated and are not included in the Elliott Bay and Eagle Harbor sites summarized here. Sources (Elliott Bay: PTI and Tetra Tech (1988), Eagle Harbor: Tetra Tech, 1986b (n=131); Non-reference areas: Tetra Tech 1986a (n=25-30).

Table 11. Sediment sites within Eagle Harbor and Elliott Bay, ranked by concentration of Total PAH (TPAH). Highest 15 out of 147 sites are shown. Boldface values are for sites adjacent to the Wyckoff facility.

Study(1)	Site	mg/kg dry wt. (ppm)			Location
		I.PAH	HPAH	TPAH	
Elliott Bay	SS-08	630	3200	3830	Seattle south waterfront
This study	W13	180	868	1048	NE of Wyckoff site
This study	W14	89	643	732	NE of Wyckoff site
This study	W15	74	457	531	NE of Wyckoff site
This study	W9	23	350	373	Under transfer area
Eagle Harbor	EH-08	128	118	246	Center of Eagle Harbor
This study	W18	53	170	223	NE of Wyckoff site
This study	W17	42	147	189	NE of Wyckoff site
Elliott Bay	NH-06	57	128	185	Near Wyckoff (Elliott Bay)
This study	W16	23	132	156	NE of Wyckoff site
Eagle Harbor	EH-10	23	108	131	Near creosote treating site
Elliott Bay	SS-09	16	102	118	Seattle south waterfront
Elliott Bay	NH-08	37	79	116	Near Wyckoff (Elliott Bay)
Eagle Harbor	EH-19	32	83	115	Near ferry shipyard
Elliott Bay	SS-06	24	77	101	Seattle south waterfront

(1) Study

Elliott Bay: PTI and Tetra Tech 1988

Eagle Harbor: Tetra Tech 1986b

CONCLUSIONS

- Very high concentrations of polycyclic aromatic hydrocarbons (PAHs) were found in sediments near the Wyckoff facility (total PAHs at one location exceeded 1000 ppm dry weight).
- Seven of 16 sample sites near the facility exceeded HPAH concentrations that can cause biological damage (as determined by comparison to highest AET).
- Concentration gradients point to Wyckoff Company (a wood treating facility) as the probable source of sediment PAHs contamination.
- Presence of PAHs and pentachlorophenol in samples from monitoring wells onsite indicate contaminants have reached the ground water.
- Comparison of relative abundance of PAHs in creosote with those in sediment and ground water onsite suggests that creosote is a source of much of the PAH found these media.

RECOMMENDATIONS

The Wyckoff site has been used for wood treating for over 50 years. It is unclear whether the contamination measured in this study is from current or historical sources. Based on the relatively high concentrations of PAH found in the environment adjacent to the Wyckoff site, the following recommendations are offered:

Clarify magnitude of ongoing contamination:

- Determine, through seepage meters and/or coring, if the high concentrations of PAHs northeast of the Wyckoff Site are caused by an ongoing seep.
- Test nearby sediments for pentachlorophenol with a more sensitive technique (EPA Method 8120).

Minimize possible ongoing sources of contamination:

- Test creosote tanks for leaks.
- Contain drips, spills, and leachate near the pole transfer area (site 9).
- Cover all areas that contain creosoted or CCA treated wood to minimize ground water contamination runoff to the bay.
- Plan response to possible spill while product is loaded into tanks.

Remediate past contamination:

- Determine feasibility of remediation of the contaminated sediment northeast of the site.

REFERENCES

- American Public Health Association (APHA), 1985. Standard methods for the examination of water and wastewater. 16 ed. Washington, DC 1,268 pp.
- EPA, 1983. Methods for chemical analysis of water and wastes.
- EPA, 1982 Test method: Inductively coupled plasma-atomic emission spectrometric method for trace element analysis of water and wastes - method 200.7. Environmental monitoring and support laboratory, Cincinnati, OH 45268.
- EPA, 1984a (Revised 1987). U.S. EPA contract laboratory program of work for organics analysis, multi-media, multi-concentrations. IFBWA 85 = T-176, T-177, T-178, U.S. EPA, Washington, D.C.
- EPA, 1984b. Guidelines establishing test procedures for the analysis of pollutants under the Clean Water Act; final rule and interim rule and proposed rule. Federal Register 49 (209):1-210.
- EPA, 1985. Puget Sound Protocols. U.S. EPA Region 10, Seattle, WA.
- EPA, 1986. Test methods for evaluating solid waste, Laboratory manual physical/chemical methods. Office of Solid Waste and Emergency Response, Washington DC SW-846.
- Goerlitz, D.F., D.E. Troutman, E.M. Godsy, and B.J. Franks. 1985. Migration of wood-preserving chemicals in contaminated groundwater in a sand aquifer at Pensacola, Florida. Environ. Sci. Technol. 19:955-961.
- Holme, N.A. and A.D. McIntyre, 1971. Methods for the study of marine benthos. Blackwell Scientific Publications, London, UK 334pp.
- Lake, J.L., C. Norwood, C. Dimock and R. Bowen. 1979. Origins of polycyclic aromatic hydrocarbons in estuarine sediments. Geochim. Cosmochim. Acta 43:1847-1854.
- Merrill, E.G. and T.L. Wade. 1985. Carbonized coal products as a source of aromatic hydrocarbons to sediments from a highly industrialized estuary. Environ. Sci. Technol. 19:597-603.
- PTI 1988. Briefing report to the EPA Science Advisory Board: The apparent effects threshold approach. Prepared by PTI Environmental Services for U.S. EPA Region 10, Seattle, WA 98101.
- PTI and Tetra Tech, 1988. Elliott Bay Action Program: Analysis of toxic problem areas. Prepared for U.S. Environmental Protection Agency. Region X, Seattle.
- Sporstol, S., N. Gjøs, R.G. Lichtenthaler, K.O. Gustavsen, K. Urdal, F. Oreld, and J. Skel. 1983. Source identification of aromatic hydrocarbons in sediments using GC/MS. Environ. Sci. Technol. 17:282-286.

- Stranks, D. W. 1976. Wood preservatives: Their depletion as fungicides and fate in the environment. Canadian Forestry Technical Report #10. Dept. of Environment, Ottawa.
- Tetra Tech. 1986a. User's Manual for Pollutants of Concern Matrix. Report to U.S. EPA, Region 10, Seattle, WA.
- Tetra Tech. 1986b. Preliminary Investigation: Eagle Harbor, Bainbridge Island, WA. Report to Washington State Department of Ecology, Olympia, WA.
- Woodward and Clyde. 1985. Contaminant data from monitor well sampling on Wyckoff Property on Elliott Bay. Analyzed by Analytical Resources Inc. available through Environmental Protection Agency, Seattle.
- Yake, B. and D. Norton. 1986. Chemical contamination of ground water, intertidal seepage and sediments on and near Wyckoff Company property; Eagle Harbor, Bainbridge Island. Memo to Glynis Stumpf and Dave Bradley, Department of Ecology, Olympia, Washington. 31pp. less attachments.

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